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Combined Use of Open-Air and Indoor Fumigation Systems to Study Effects of SO₂ on Leaching Processes in Scots Pine Litter

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ABSTRACT

Both an open-air fumigation system and a laboratory-based system were used to expose decomposing Scots pine (Pinus sylvestris L.) needles to controlled concentrations of SO₂ (arithmetic mean ≤ 48 nl litre⁻¹) during a period, in total, of 301 days. The experimental design involved reciprocal litter transplants from 'clean' to 'polluted' air and vice versa, using the two fumigation systems. The objectives were (1) to observe the effects of SO₂ on leachate and litter chemistry, (2) to assess whether pollution-induced changes are reversible in clean air, and (3) to test the suitability of small-scale fumigation chambers (litter microcosms) compared with open-air systems in soil studies.

Through the formation of SO₄²⁻ ions, dry-deposited SO₂ exhibited a marked capacity to remove 'base' cations (Ca²⁺, Mg²⁺ and K⁺) from decomposing pine needles, and also to acidify litter leachates (as indicated by proton fluxes from the litter). When litter was transferred from polluted air (48 nl litre⁻¹ SO₂, in the open-air system) to either clean or

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polluted air in the laboratory, the effects of prior exposure to SO₂ on leachate composition were still evident even after 86 days: the role of base cation depletion within the litter, caused by SO₄²⁻-induced leaching, is discussed.

Data for SO₄²⁻ fluxes in leachates collected from the small-scale chambers indicated that dry deposition velocities for SO₂ were not anomalously high within this fumigation system. It is therefore concluded that microcosm studies can provide information complementary to the open-air fumigation approach in soils research.

INTRODUCTION

Dry deposition of SO₂ has been implicated as a major factor contributing to the acidification of soils and freshwater systems in Europe (van Breemen *et al.*, 1984; Paces, 1985), and there is now a wealth of data emphasizing the quantitative significance of dry deposition, relative to wet ('acid rain'), over considerable areas closer to emissions sources (Moss, 1978; UK Review Group on Acid Rain, 1987; Williams *et al.*, 1989). Indeed, the United Kingdom Review Group on Acid Rain (1987) has stated that, in broad terms, dry deposition may exceed wet in those regions where atmospheric SO₂ concentrations exceed 3.8 nl litre⁻¹. The data of EMEP (1984), and Williams *et al.* (1989), provide clear evidence that this concentration has been exceeded over much of central Europe (mainly in Germany, The Netherlands and western regions of Czechoslovakia) and central and eastern England.

Unfortunately, the major significance of dry-deposition fluxes to terrestrial ecosystems has not prompted an equivalent research effort. There have thus been few attempts to determine, in controlled experiments, whether the dry deposition of pollutant gases (notably SO₂ and NO₂) directly to litter and soils could have a significant ecological impact. Experiments are needed, none the less, in order to better understand the relationship between specific concentrations of atmospheric SO₂, deposition fluxes, and the associated acidification reactions.

Dry-deposited SO₂ has a greater capacity to cause acidification than an equivalent input of wet-deposited sulphur (as sulphate) in acid rain. This arises because inputs of gaseous SO₂ to terrestrial or freshwater ecosystems carry no neutralizing capacity, this being in contrast to the situation with wet-deposited SO₄²⁻. The sulphate component of acid rain is balanced not only by H⁺, but also by 'base' cations such as Ca²⁺ and K⁺ (EMEP, 1984; Lindberg *et al.*, 1986). The presence of NH₄⁺ ions in rainfall, though contributing to neutralization, may ultimately represent an

input of acidity to soil systems upon oxidation to NO₃⁻ (van Breemen *et al.*, 1984).

Fluxes of SO₂ to forested ecosystems remain a subject of intense debate. Particular attention has focussed on canopy interactions, and the relative significance of foliar leaching and dry deposition to the sulphur content of canopy throughfall (Lindberg & Garten, 1988; Gay & Murphy, 1989; Puckett, 1990). The major significance of dry deposition to forest canopies, both to external plant surfaces and via the stomata, does not, however, indicate that dry-deposited SO₂ has only limited impacts on forest soils; indeed, Garland and Branson (1977) stressed that much of the sulphur dry-deposited to canopies 'must eventually reach the forest floor as sulphate'.

The research described in this paper relates specifically to the effects of dry-deposited SO₂ on chemical events occurring in Scots pine (*Pinus sylvestris* L.) litter. In this study, decomposing pine needles were exposed to controlled SO₂ concentrations, first in an open-air and then subsequently in a laboratory-based fumigation. The results of the open-air experiment are described in full elsewhere (Wookey *et al.*, 1991; Wookey & Ineson, in press), although they are outlined briefly here because they are of central importance for the interpretation of the laboratory studies.

In the open-air experiment decomposition processes—both biotic (performed by decomposer organisms) and abiotic (aqueous leaching processes involving ion exchange reactions)—were altered by exposure to SO₂ concentrations (arithmetic mean values of 15 nl litre⁻¹ the lowest concentrations tested) similar to those known to occur over substantial areas of industrialized Europe (see Martin, 1980; Lefohn & Mohnen, 1986; Ling & Ashmore, 1987). The most notable observations included a marked reduction in microbial respiration (an index of catabolic processes), greater acidification of decomposing pine needles and an increased leaching loss of the divalent cations Ca²⁺ and Mg²⁺ in association with higher SO₂ concentrations. The leaching of divalent cations occurred in response to enhanced SO₄²⁻ leaching.

The very marked effects of SO₂ on decomposition processes, as demonstrated in the open-air fumigation experiment, prompted a laboratory-based fumigation study which sought: (1) to complement the open-air studies by providing information on *cumulative* fluxes of SO₄²⁻, H⁺, Ca²⁺, Mg²⁺ and K⁺ from pine litter over time (the open-air studies described above only provide instantaneous measurements of fluxes); (2) to evaluate the changes in chemical composition of leachates when litter was moved from 'polluted' to 'clean' air; and (3) to indicate whether the kinds of results obtained during open-air studies could also be obtained under artificial conditions in the laboratory. Open-air fumigation systems are

costly to build and maintain, and few such systems exist; the possibility of using smaller-scale, and considerably less complex, laboratory-based systems to complement results from open-air studies is therefore attractive.

In the study described here these questions were considered by collecting pine litter from the open-air fumigation system after 215 days of exposure to either ambient ('control') air, or air to which additional SO₂ had been added ('polluted'). Each of these two litter samples was then subdivided and subsequently exposed to either charcoal-filtered air or to artificially polluted air—with similar arithmetic mean SO₂ concentrations to the open-air 'polluted' treatment—in a laboratory-based fumigation system.

MATERIALS AND METHODS

Open-air fumigation of Scots pine needle litter

A full technical description of the open-air fumigation system can be found in McLeod *et al.* (1991). The system was designed, constructed and maintained by staff of the Central Electricity Research Laboratory (now the National Power Technology and Environmental Centre (NPTEC), Leatherhead, UK, and was sited at the Institute of Horticultural Research, Littlehampton, Sussex. The system consisted of four field plots, one receiving ambient SO₂ exposure (generally less than 10 nl litre⁻¹ as an annual mean). The remaining three plots contained dispersion pipework to allow enrichment of the atmosphere immediately above them with SO₂.

Scots pine (*Pinus sylvestris* L.) litter, for use in the open-air fumigation, was collected from the litter (L) layer of the forest floor in a 32-year-old stand at Gisburn Forest, Lancashire (G.R. SD 750588). This was then air-dried prior to transportation and placement at the open-air site (see Wookey *et al.*, 1991 for full details of procedures). The pine litter was exposed to the four contrasting SO₂ regimes for a period of 215 days in total.

Litter collected from the open-air site was analyzed for rates of CO₂ release (microbial respiration) (Wookey *et al.*, 1991), chemistry of leachates, and needle calcium, magnesium, potassium and nitrogen contents (Wookey & Ineson, in press).

Transfer of *Pinus sylvestris* litter from the open-air fumigation experiment to the laboratory-based fumigation system

The first litter set was removed from the ambient (control) plot and had been exposed to a mean SO₂ concentration of 7 nl litre⁻¹. The other set

came from the plot with the highest arithmetic mean concentration of SO_2 , 48 nl litre^{-1} .

Each of the two litter samples was used to prepare six 'microcosm chambers' (Fig. 1), based on the design of Anderson and Ineson (1982). Six chambers thus contained pine needles from the ambient open-air plot, and six contained needles from the $48 \text{ nl litre}^{-1} \text{ SO}_2$ plot. The microcosm chambers were designed to allow decomposition processes to be studied under carefully controlled environmental conditions. Such chambers proved appropriate both for SO_2 fumigation work, and also the examination of leachate solutions, without causing undue disturbance of the decomposing litter. The microcosm system also enabled experimental treatments to be replicated.

Fresh litter was used for the microcosms, although the equivalent oven-dry weights—estimated by drying subsamples of litter and then applying the appropriate conversion factor—ranged from 1.46 to 1.94 g per microcosm. Once filled with litter, each of the microcosm chambers was thoroughly moistened with a 100 ml aliquot of deionized water, which was then allowed to drain away, before being connected to the laboratory-based fumigation system (described in full in Wookey *et al.*, 1991).

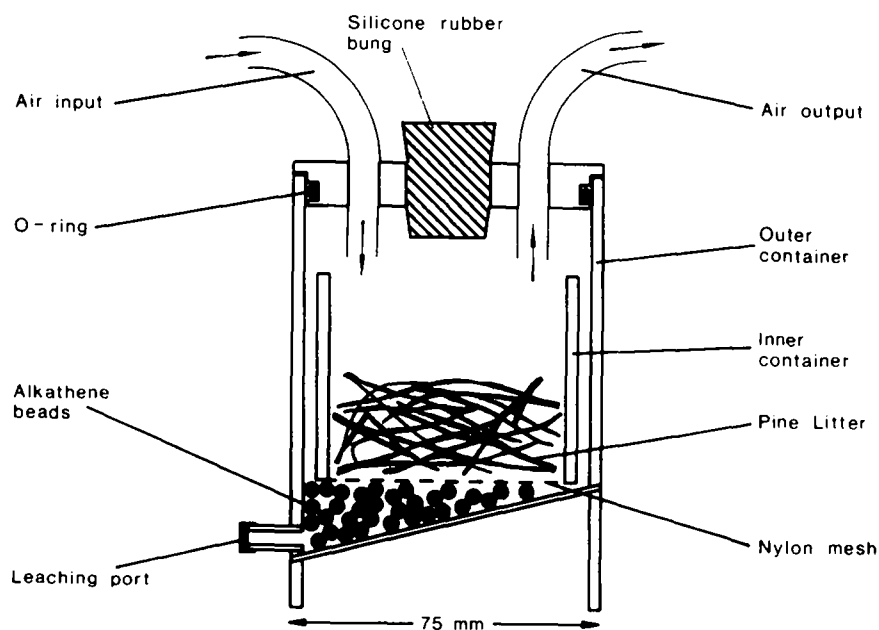


Fig. 1. Microcosm chamber (working volume 0.33 litres), adapted from a design by Anderson and Ineson (1982), and constructed principally from clear perspex sheet and cylinders. Twelve such microcosm chambers were used for the laboratory-based fumigation. During fumigation the leaching port remained sealed.

TABLE 1

Outline of the SO₂ Concentrations to which *P. sylvestris* Needles were exposed in the Open-Air Fumigation and Subsequently the Laboratory System

Treatment identity	Abbreviation	No. of replicate microcosms	SO ₂ concentration (nl litre ⁻¹)	
			For 215 days in open-air fumigation	For 86 days in laboratory based system
Control-control	CC	3	7	2
Control-polluted	CP	3	7	47 ^a
Polluted-control	PC	3	48	2
Polluted-polluted	PP	3	48	47 ^a

^a In the laboratory system the SO₂ supply was switched off for 19% of the time (for the collection of leachates, and for other analyses). The SO₂ concentration quoted here is the arithmetic mean value only for the period during which the SO₂ supply was on (70 out of 86 days). When the value is recalculated to show mean SO₂ concentration during the complete 86 day period the figure becomes 38 nl litre⁻¹.

Table 1 provides a summary of the SO₂ regimes, both in the open-air fumigation system and in the laboratory-based system, to which the Scots pine litter was exposed. Of the six microcosms containing litter exposed to 7 nl litre⁻¹ SO₂ in the open air, three were subsequently placed in the 'SO₂-free' (control) airstream (corresponding to treatment 'CC'), the other three were exposed to an airstream containing a mean of 47 nl litre⁻¹ SO₂ (treatment 'CP'). Of the six microcosms containing litter exposed to 48 nl litre⁻¹ SO₂ in the open air, three were placed in the SO₂-free airstream (treatment 'PC'), and the other three were exposed to 47 nl litre⁻¹ SO₂ (treatment 'PP').

The laboratory-based fumigation system

The air supply entering the laboratory-based fumigation system (5.2 litre min⁻¹ of outside air) was filtered through activated charcoal (8/12 mesh), contained within a column, 445 mm long and 65 mm diameter, and subsequently humidified by bubbling through deionized water. The airstream was then split into 13, and SO₂ was added to the six 'polluted' airstreams to give the desired concentration (Wookey *et al.*, 1991). Of the seven 'SO₂-free' airstreams, one was passed through an empty 'reference' microcosm chamber in order to provide a 'blank' for analytical purposes.

All 13 microcosms were housed within an incubator (15.8 °C) and air-

flow rates through each of them were maintained at *c.* 0.4 litre min^{-1} . A Meloy Model SA 185-2 flame photometric detection sulphur analyzer (Meloy Laboratories Inc., Springfield, VA) was used to measure SO_2 concentrations of air entering each microcosm chamber. This was calibrated using sulphur hexafluoride (SF_6) in air (BOC Special Gases, London) at a concentration of 85 nl litre $^{-1}$.

Sulphur dioxide concentrations for the laboratory-based system (see Table 1) were monitored at the *input* to the microcosms, since this was the sampling point at which effective control could best be exerted. In view of the small volume of the microcosm chambers (0.33 litre working volume), the authors consider that input concentrations were appropriate, although with larger chambers, in which the air is also well mixed, it is generally accepted that *output* concentrations are most representative of conditions within the chamber (Koziol, 1980; Unsworth & Mansfield, 1980).

The laboratory-based component of the SO_2 fumigation commenced two days after the litter microcosms were established and lasted exactly 12 weeks thereafter; leachates were collected for chemical analyses every two weeks. During leachate collection each microcosm in turn was disconnected from the fumigation system, the silicone bung removed from the lid (Fig. 1) and the litter then flooded with 100 ml of deionized water. The resulting leachates were removed via the leaching port and retained for chemical analyses. SO_4^{2-} was analyzed by chemically suppressed ion chromatography (Dionex), H^+ (pH) using a combination electrode, Ca^{2+} and Mg^{2+} by atomic absorption spectrophotometry, K^+ by flame emission spectrophotometry, and $\text{NH}_4^+\text{-N}$ using an auto-analyzer (Berthelot reaction). Fluxes of ions from the litter were expressed as μ -equivalents leached g^{-1} litter. Analyses were confined to litter leachates only and did not include an examination of the litter material itself.

During the course of the fumigation, the needles in the microcosms were occasionally moistened with small and equal-measured aliquots of deionized water, to prevent excessive drying. SO_2 concentrations were, as far as possible, held constant, this being in marked contrast to the situation in the open-air fumigation where the large temporal fluctuations in SO_2 concentrations better represented the situation in the polluted environment (McLeod *et al.*, 1985). SO_2 concentrations during the laboratory-based fumigation were, as far as possible, monitored daily and adjusted when necessary.

RESULTS AND DISCUSSION

Results are presented graphically in Figs 2–4. Statistical significance of the data was assessed by means of one way analysis of variance and

Tukey's comparison of means test for each sampling occasion. The leachate compositions for day zero have been taken from results for the second sampling date (11 July 1986) of the open-air experiment (see Wookey & Ineson, in press).

Figures 2 and 3 show SO_4^{2-} leaching from the pine needles during the laboratory-based fumigation. At day zero, two days before the SO_2 was switched on, the quantity of SO_4^{2-} leached from needles previously exposed to $48 \text{ nl litre}^{-1} \text{ SO}_2$ in the open-air amounted to four times as much as was leached from needles exposed to $7 \text{ nl litre}^{-1} \text{ SO}_2$ (ambient air). However, 14 days after the start of fumigation (day 16) sulphate release from 'CP' needles had risen sharply to match that of the 'PP' needles. Subsequently, leaching was high from all the microcosms exposed to $47 \text{ nl litre}^{-1} \text{ SO}_2$ in the laboratory-based system.

If not immobilized by microorganisms, SO_2 deposited to leaf litter and soils will ultimately oxidize to SO_4^{2-} under moist conditions (Lockyer

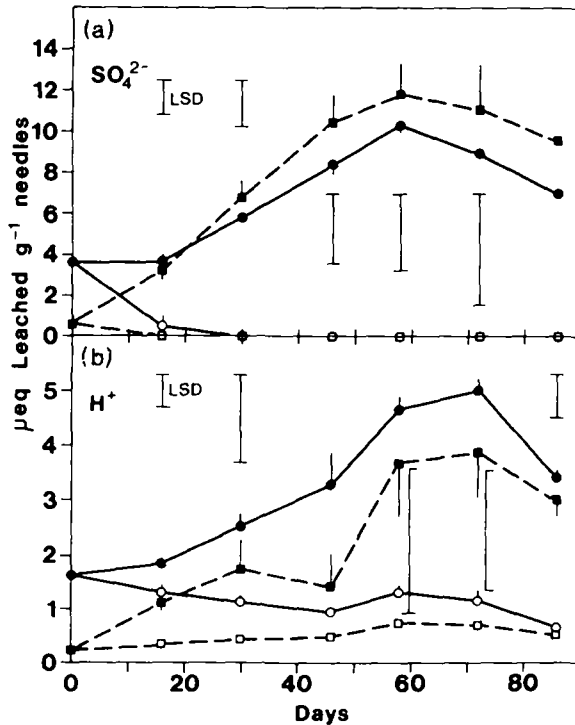


Fig. 2. Leachate composition of *P. sylvestris* needles (μ -equivalents leached g^{-1} needles) plotted against time (days) since the beginning of the laboratory-based fumigation experiment. Means (± 1 standard error) are joined by lines. Statistical significance indicated by least significant difference (LSD), Tukey's comparison of means test ($P < 0.05$).

Treatments: CC, \square ; CP, \blacksquare ; PC \circ ; PP, \bullet .

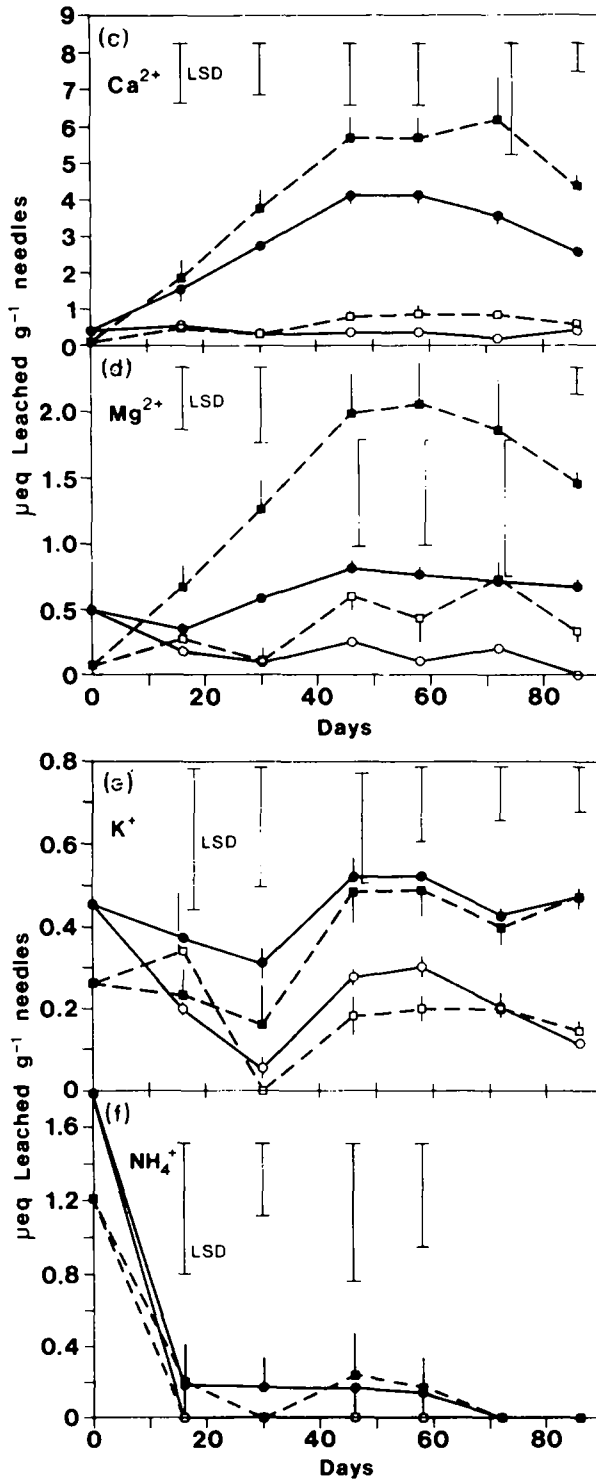


Fig. 2.—contd.

et al., 1978; Lettl, 1984). Chemical transformations leading to sulphate formation in aqueous phase have been considered by Brimblecombe (1978), Davies (1979), Babich and Stotzky (1980) and Cape (1984). The subsequent fate of SO_4^{2-} ions, originating from both wet and dry deposition from the atmosphere, is of central importance in understanding acidification reactions both in soils and in freshwater ecosystems (Tamm, 1976; Krug & Frink, 1983; Abrahamsen, 1984; Johnson & Reuss, 1984; Morrison, 1984; Reuss *et al.*, 1987).

No sulphate (or rather quantities below the analytical detection limit of $1.1 \mu\text{-equivalents g}^{-1}$ litter) was leached from pine needles exposed to

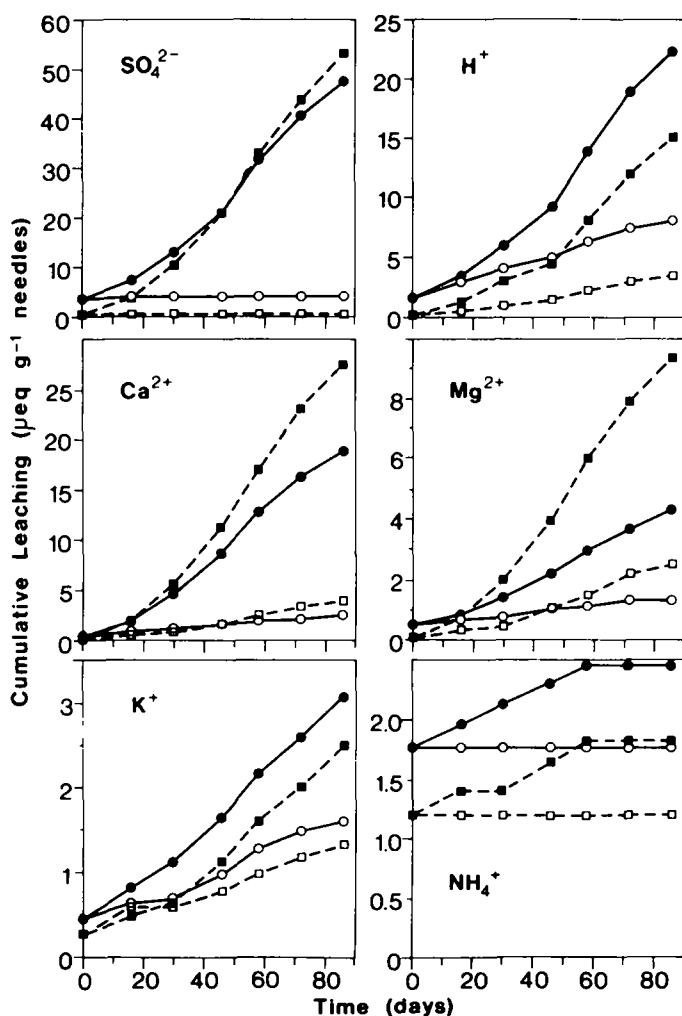


Fig. 3. Cumulative leaching from *P. sylvestris* needles, plotted against time (days) since the beginning of the laboratory experiment. Treatments as for Fig. 2.

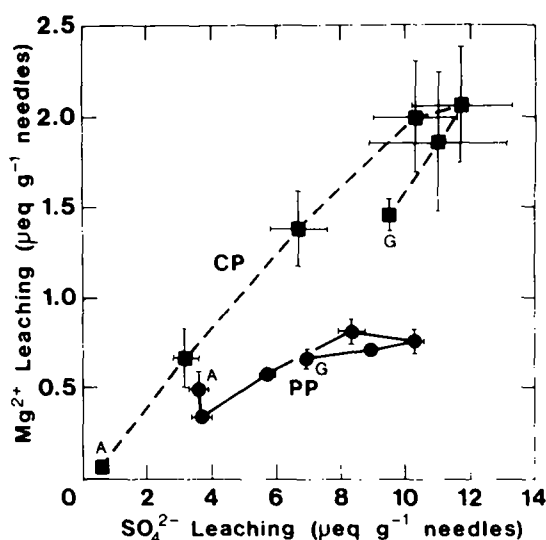


Fig. 4. Mg^{2+} leaching plotted against SO_4^{2-} leaching for CP (■); and PP (●) treatments. Means (± 1 standard error) are joined by lines. The points marked 'A' show leachate composition at the start of the laboratory-based fumigation, while those marked 'G' show the final values.

' SO_2 -free' air (actually 2 nl litre⁻¹ SO_2) in the laboratory system, with the exception of the PC needles which still lost a small amount of residual SO_4^{2-} up to day 16. These results suggest that microbial mineralization of organically bound sulphur in the pine needles did not contribute significantly to leachate SO_4^{2-} fluxes during the course of this experiment.

The general increase in SO_4^{2-} leaching from needles exposed to 47 nl litre⁻¹ SO_2 in the laboratory (CP and PP) compared with needles exposed to 48 nl litre⁻¹ in the open-air fumigation (leaching on day 0 for PC and PP needles) may be explained by the contrasting nature of environmental regimes and sampling procedures in the open air and in the microcosm chambers. Needles exposed to SO_2 in the open will have been 'leached' naturally by rainfall, which much of the dry-deposited sulphur present on the needle surfaces prior to any rainfall event presumably being removed in the percolating rainwater. Thus, in the open air the amount of SO_4^{2-} leached from the needles at any particular time will be a function not only of the recent deposition flux but also of the time elapsed since the last rainfall event. Since the sampling dates for the open-air fumigation were not chosen with respect to rainfall, the amounts of SO_4^{2-} leached from the needles therefore indicate *relative* differences between SO_2 regimes only, and do not represent absolute fluxes to the needles, being valid only for a particular moment in time.

The laboratory system contrasted in two ways with the open-air system. First, needles in microcosm chambers were not exposed to rain-washing events. Needles were moistened regularly between leachate collections with small aliquots of deionised water (to prevent excessive drying), but this treatment was considered insufficient, relative to a rainfall event, to wash a significant amount of SO_4^{2-} from the needle surfaces (quantities of deionized water were selected to avoid accumulation of excess liquid at the base of microcosms). Thus, in the laboratory, the surfaces of needles exposed to SO_2 will have been in contact with contrasting absolute concentrations and temporal patterns of SO_4^{2-} relative to needles exposed in the open air. Only the fortnightly leaching with deionized water could have simulated the type of SO_4^{2-} removal associated with a rainfall event. The second major difference concerns the fact that values for SO_4^{2-} leaching obtained from the laboratory fumigation represented SO_4^{2-} production over the whole of the time period which had elapsed since the previous leaching. It is therefore possible that leachate sulphate fluxes from the litter could provide an indication of the dry-deposition fluxes of SO_2 , although the possibility of microbial mineralization of organically bound sulphur in the litter contributing to the leachate SO_4^{2-} should not be overlooked.

The oxidation of SO_2 to SO_4^{2-} —the mobile anion of a strong acid (Reuss *et al.*, 1987)—can be expected to have profound implications for a number of chemical reactions occurring at litter surfaces, and also lower down a soil profile. The generation of SO_4^{2-} will tend to promote acidification reactions by encouraging the formation of H^+ ions (protons) to maintain charge balance (Nyborg, 1978; van Breemen *et al.*, 1984; Paces, 1985). These protons can then enter into exchange reactions with cations held on negatively charged sites in litter layers of mineral soil. 'Base' cations such as Ca^{2+} , Mg^{2+} , Na^+ or K^+ , or the 'acid' cations Al^{3+} , which are electrostatically bound to organic or mineral particles, can thus be released into solution and made available for leaching. This provides a means for buffering H^+ ions associated with anions in solution: the existence of such cation exchange processes can be clearly demonstrated in the present study by comparing the results for sulphate leaching, expressed on a charge equivalence basis, with those for the leaching of base cations, and also protons.

Sulphate present in litter leachates was not entirely balanced in charge by an equivalent formation of protons. Indeed, proton formation balanced less than half the SO_4^{2-} , the remainder of the positive charge being provided principally by the cations Ca^{2+} , Mg^{2+} , K^+ and NH_4^+ (Figs 2 and 3).

Leaching rates of the divalent cations during the laboratory-based fumigation reflected not only the SO_2 concentration of the air but also

the 'pool size' of the element in question. On an equivalence basis, Ca²⁺ was the most significant cation. If the calcium content of the needles, after 215 days of exposure to 7 nl litre⁻¹ SO₂ in the open air, was the same as that of needles exposed to 48 nl litre⁻¹ then the subsequent laboratory treatment may have been expected to yield magnitudes to Ca₂⁺ leaching in proportion to SO₄²⁻ leaching. Clearly the response pattern was different, with PP needles losing 31% less calcium than the CP needles by the end of the laboratory-based fumigation (Fig. 3). These results are readily explained by the observation (Wookey & Ineson, in press) that exposure to 48 nl litre⁻¹ SO₂ for 156 days in the open air resulted in a reduction in needle calcium contents (Table 2: Ca, Mg and K contents of litter). At the start of the laboratory-based fumigation the PP needles probably (see footnote to Table 2) contained a more heavily depleted calcium pool than the CP needles, thereby leading to a lower availability of Ca²⁺ for SO₄²⁻ mediated leaching. Further support for the hypothesis is provided by comparing calcium leaching (Figs 2(c) and 3) from the CC and PC needles.

Data for Mg²⁺ leaching during the laboratory-based part of this experiment showed the same patterns as Ca²⁺, except that the cation depletion effect was even more clearly evident (Figs 2(d) and 4, and also Table 2). The cumulative leaching of Mg²⁺ from the CP needles after 86 days in the laboratory system amounted to 115% more than that leached from the PP needles (Fig. 3); this pattern is further highlighted by plotting Mg²⁺ leaching from CP and PP needles against SO₄²⁻ (Fig. 4). Magnesium

TABLE 2

Element Analyses (% dry weight) for Litter Bag Samples Collected After 156 Days of Exposure in the Open-Air Fumigation Experiment. Means of six replicate Samples are given. Differences between SO₂ Treatments Statistically Significant ($P < 0.01$) for All Elements

Treatment	Element		
	Ca	Mg	K
Ambient SO ₂ (8 nl litre ⁻¹)	0.312 (0.11) ^a	0.058 (0.002)	0.106 (0.007)
High SO ₂ (50 nl litre ⁻¹)	0.140 (0.004)	0.031 (0.001)	0.077 (0.003)

^aStandard error in parentheses.

Note: Values given here refer to litter composition 59 days prior to collection date of litter for use in the laboratory-based fumigation study (litter bag samples collected after 215 days were used for microbiological studies and could not, therefore, be analyzed in the same way; see Wookey *et al.* (1991)).

loss from the PC needles was very low over the course of the experiment and reached 'zero' (below the analytical detection limit of $0.1 \mu\text{-equivalents g}^{-1}$ litter) after 86 days.

The same type of leaching pattern was not found for K^+ compared with Ca^{2+} or Mg^{2+} (Figs 2(e) and 3): the data for K^+ show no sign that leachable potassium reserves were appreciably depleted in litter exposed to $48 \text{ nl litre}^{-1} \text{ SO}_2$ in the open-air compared to the 7 nl litre^{-1} control. This is in direct contrast with the actual results of needle analyses (Table 2) which show a statistically significant reduction in potassium content of litter exposed to $50 \text{ nl litre}^{-1} \text{ SO}_2$ compared with the control ($8 \text{ nl litre}^{-1} \text{ SO}_2$). It should be emphasized, however, that the litter analyses of the open-air fumigation were performed after 156 days of exposure, rather than after 215 days, and the K content of the needles may have changed appreciably during the intervening 59 days.

Ammonium leaching rates were very low in the laboratory-based system (Figs 2(f) and 3) and rapidly declined to below the detection limit ($0.43 \mu\text{-equivalents g}^{-1}$ litter) in all of the microcosm chambers exposed to clean air (CC and PC). Conversely, small quantities of NH_4^+ were still detected until day 72 in leachates removed from some, but not all, of the 'polluted' chambers (this resulted in mean values lower than the analytical detection limit and not significantly different from zero; $P > 0.05$). It is likely that charcoal filtration of the air entering the laboratory system removed a substantial proportion of the gaseous ammonia present in ambient air (Dueck, 1990) and this, in turn, may have limited both the dry deposition of NH_3 to pine litter and the subsequent formation of NH_4^+ . Such a mechanism could also explain the very marked reduction in NH_4^+ leaching when litter was transferred from the open-air (Fig. 2(f) 'Time 0') to the laboratory-based system. It is of interest that NH_4^+ leaching could be detected only from microcosms exposed to $47 \text{ nl litre}^{-1} \text{ SO}_2$ in the laboratory, and these results may indicate that the acidification of polluted litter (see below) enhanced the deposition of residual NH_3 still present in the airstream after filtration. The data are consistent with the phenomenon of co-deposition of SO_2 and NH_3 (McLeod *et al.*, 1990), although the lack of statistically significant differences between treatments in this study, together with leaching rate close to (or below) the analytical detection limits, places restrictions on this interpretation.

Base cation and ammonium leaching was insufficient to completely buffer the SO_4^{2-} present in leachates and, as expected, protons provided the remainder of the charge balance. Leachate analyses indicated that needle material exposed to $47 \text{ nl litre}^{-1} \text{ SO}_2$ in the laboratory system was acidified compared with needles exposed to SO_2 -free air. The close association between proton formation and the degree of base cation (calcium

and magnesium) depletion of the needles is clearly indicated by the results (Figs 2 and 3). Needles exposed to $48 \text{ nl litre}^{-1} \text{ SO}_2$ in the open-air initially leached more H^+ ions (had a lower pH; values ranging from a pH of 4.0 to 4.4) than needles exposed to ambient air (pH 5.0–5.3). This was attributed to enhanced SO_4^{2-} formation in the needles exposed to higher SO_2 concentrations. When needles were taken from an open-air environment containing $48 \text{ nl litre}^{-1} \text{ SO}_2$ and then placed into an airstream containing $47 \text{ nl litre}^{-1} \text{ SO}_2$ in the laboratory system, the formation of protons remained high, due both to high SO_4^{2-} concentrations occurring as a consequence of SO_2 deposition, and also the high degree of cation depletion resulting in a low SO_4^{2-} buffering capacity.

The results for CP needles were quite different and can be explained on consideration of the higher base status of the needles before the laboratory-based component of SO_2 exposure. In spite of higher SO_4^{2-} leaching from the CP needles compared with the PP needles, there was actually less H^+ ion formation in the former, probably because more of the SO_4^{2-} was balanced by cation leaching, especially of Ca^{2+} (Fig. 3). Needles exposed to SO_2 -free air in the laboratory system support this hypothesis since, although SO_4^{2-} leaching quickly dropped to undetectable amounts from the PC needles, these needles still leached more H^+ ions than the CC needles, even after 86 days, indicating that their buffering capacity was lower than the CC needles.

The use of small microcosm chambers within a laboratory-based fumigation system enabled fluxes of ions in leachates to be assessed regularly, and the results to be related to specific concentrations of gaseous SO_2 under carefully controlled conditions. The laboratory-based system can therefore be used to provide high-resolution data which can supplement results from open-air studies. It is important to recognize, however, that the artificial environmental conditions within the microcosm chambers may have resulted in unrealistic deposition fluxes of SO_2 to the litter. This was tested by estimating the deposition velocity (V_g) of SO_2 to the pine litter on the basis of SO_4^{2-} fluxes (see Wookey (1988) for details of methods).

Estimates of V_g ranged from 1.2 to 1.3 mm s^{-1} , these values probably representing an upper limit, and this compares favourably with values reported for a range of soils, coniferous forest canopies, and for a senescent cereal crop (Lockyer *et al.*, 1978; Fowler 1980, 1985). Ineson (1983) measured V_g to the litter layer of a recently felled *P. sylvestris* stand and found values ranging from 2 to 2.5 mm s^{-1} . V_g values did not, therefore, seem to be unusually high within the laboratory-based system: viewed in conjunction with the data on cation leaching from the litter, they provide a very striking indication of the capacity of dry-deposited SO_2 to bring about chemical changes.

CONCLUSIONS

Both the open-air and the laboratory-based fumigation studies illustrated the marked capacity for dry-deposited SO_2 to alter the nature of chemical reactions within decomposing *P. sylvestris* litter. Exposure to arithmetic mean SO_2 concentrations of 47 nl litre^{-1} for 70 days (out of 86 days), using the microcosm chamber system, enabled cumulative fluxes of SO_4^{2-} , H^+ , NH_4^+ and base cations within the leachates to be assessed. Sulphate formation—in response to the dry deposition of SO_2 —provided the mobile anions, and associated protons, to initiate cation exchange reactions within the litter: in this way Ca^{2+} , Mg^{2+} and K^+ were made available for removal by leaching. More than half of the negative charge associated with SO_4^{2-} leaching was balanced by Ca^{2+} plus Mg^{2+} .

Reciprocal litter transplants, using the two fumigation systems, indicated that pollution-induced changes in leachate chemistry were not immediately reversible in clean air. Leachates collected from litter previously exposed to 48 nl litre^{-1} SO_2 for 215 days in the open-air, and then subsequently to 2 nl litre^{-1} in the microcosm system ('PC' treatment), showed evidence of base cation depletion (particularly Ca^{2+} and Mg^{2+}) during the open-air fumigation. The leachates also remained slightly acidified (compared with the CC controls) for much of the 'clean air' exposure (86 days) even though SO_4^{2-} fluxes rapidly declined to below the analytical detection limit. Leachates collected from the PP (polluted–polluted) treatment provided particularly striking evidence of base cation depletion associated with SO_4^{2-} leaching.

Estimates of the deposition velocity (V_g) of SO_2 to litter within the microcosm system ($1.2\text{--}1.3 \text{ mm s}^{-1}$) gave values well within the range reported by other workers, and it is concluded that microcosm studies can provide a valid supplement to the open-air fumigation approach. Laboratory-based microcosm systems cannot reproduce, however, the complex fluctuations in air pollutant concentrations and environmental conditions encountered in the open-air: and for this reason they should not be considered a complete replacement for open-air fumigation systems.

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